



Translation #SU2230

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The invention concerns porous, corrosion-proof, non-electrically-conducting partitions, consisting of oxide ceramic-coated metal nets, which are particularly suited as diaphragms and filters for the operation of electrolyzers as well as for materials separation and filtration in acidic, neutral and alkaline solutions.

Corrosion-proof diaphragms and filters made of oxide ceramic-coated metal nets are known from *Chemie Ing. Technik* 52, (1980), No. 5, pages 438 to 439. The oxide ceramic consists of mixed oxides of bivalent alkaline earth metals and transition metals such as metals from Group IVA and VA of the periodic system. A disadvantage of these diaphragms and filters is the poor adhesion of the oxide ceramic on the metal net. If the ceramic coating is damaged, it crumbles away easily from the metal net.

Porous oxide diaphragms for alkaline water electrolytes are known from EP-A-00 46 252, in which the oxide layer supported by net-like or sieve-like carriers maintained by oxidation of metallic powder particles, which are applied to the carrier by cold compression.

The problem is therefore presented of creating diaphragms and filters supported by metal nets that exhibit an intimate bond between ceramic and metal net, and thus better mechanical stability.

The problem is solved by having the oxide ceramic coating contain metal particles in amounts from 15 to 75 weight %, relative to the weight of the oxide ceramics. The average pore diameter of the oxide ceramics can be from 5 to 50 μm . The oxide ceramics may contain mixed oxides consisting of the oxides of alkaline earth metals and amphoteric oxides of the metals group IVA, VA or VIA of the Periodic Table. The mixed oxides should preferably consist of alkaline earth titanate. The metal particles may consist of metals of group IVA or VIII of the Periodic Table.

The term mixed oxides refers here to mixtures of several oxides as well as compounds of several oxides, i.e. double oxides or triple oxides.

Particularly suited as oxide ceramic components of the ceramics are compounds on the one hand of oxides of calcium, strontium, barium, or on the other hand of amphoteric oxides of titanium, zirconium, hafnium, niobium, tantalum, molybdenum and/or tungsten. As metallic components of the ceramics as well as for the metal net, nickel, titanium and zirconium are particularly suited.

In order to manufacture the porous partitions, a pre-mixture of metal oxides and metal particles needed for the ceramics is applied to a metal net. In place of the pure metal particles, the corresponding oxide may also be used, provided that it can be reduced to metal under the manufacturing conditions for the partitions. In order to attain the desired average pore diameter, the components for the pre-mixture, i.e. the oxides and the metals may be milled either together or separately and assembled in sifted fractions. The pre-mixture in the form of a bonding paste may be painted, printed or applied to the metal net in some other suitable manner with the desired coating weight. Following this the bond is heated and the partitions are sintered at temperatures below the melting point of the metallic components in reducing or inert atmosphere (CO , H_2 or N_2).

Example 1

A mixture containing 50 weight % nickel powder 50 weight % nickel-titanate with an average particle size of $5\mu\text{m}$ was sintered at 1100°C for 4 hours. The thus-sintered body was pulverized and milled in a ball mill. The material to be milled was separated into various fractions using sieves, with the fractions having particle sizes of $\leq 5\mu\text{m}$, $\leq 20\mu\text{m}$, $\leq 50\mu\text{m}$. From these three fractions, the following mixtures for samples a), b), c) were produced:

| | | | |
|------------------------------------|-----------------|----------------|----------------|
| Particle size: $\leq 5\mu\text{m}$ | a) 100 weight % | b) 60 weight % | c) 50 weight % |
| $\leq 20\mu\text{m}$ | - | 40 weight % | 30 weight % |
| $\leq 50\mu\text{m}$ | - | - | 20 weight % |

A printable paste was made from sample a) through mixing with a 5 weight % carboxymethylcellulose-containing solution, and using a screen printing process, a nickel net with 0.34 mm mesh size and 0.25 mm wire gauge was printed on both sides in three passes each.

The "green" partition was dried and, after thermal disintegration of the organic bond at 1100°C for 45 minutes under an H_2/N_2 atmosphere, in which the H_2/N_2 was 30:70, sintered in a chamber oven. Using samples b) and c), a paste was made from each one by mixing with a mixture of 80 weight % linseed oil and 20 weight % butanol, and each was painted onto a nickel net as with sample a). The "green" partitions were dried and, after thermal disintegration of the bond, sintered in a chamber oven; sample b) for two hours at 1100°C under an H_2/N_2 atmosphere, in which the H_2/N_2 was 40:60; and sample c) at 1200°C under an H_2/N_2 atmosphere, in which the H_2/N_2 was 50:50.

The surface resistance of the partitions produced in this manner is approx $400\text{ m}\Omega\text{cm}^2$ at 25°C in 50 weight % KOH; the dynamic transmission approx $0.5\text{ cm}^3\text{ poise/bar cm}^2$. The partitions are short circuit proof at a voltage of 120 volts.

Example 2

A mixture of 35 weight % nickel oxide and 65 weight % barium titanate was sintered as in Example 1, pulverized, milled and sifted. The powder mixture, of which the maximum particle size was $\leq 50\mu\text{m}$, was pasted with a 2% sucrose solution and the paste applied to a nickel net with 0.52 mm mesh size and 0.3 mm wire gauge. The coated net was pre-hardened by slow heating in a chamber oven under an air atmosphere and the sucrose carbonized. Then it was sintered under H_2 atmosphere for 75 minutes at approx 1400°C and cooled down over the course of 2 hours to 600°C . The surface-specific resistance of the partition thus produced is approx $300\text{ m}\Omega\text{cm}^2$ at 25°C , the hydrodynamic transmission $0.55\text{ cm}^3\text{ poise/bar cm}^2$. The oxide ceramic adheres well to the carrier net. It does not crumble away easily under mechanical damage. The partition is short circuit proof at a voltage of 100 volts.